

Improvement of Adhesion Properties of Fluorinated Silica Glass Films by Nitrous Oxide Plasma Treatment

Richard Swope,* Woo Sik Yoo,* Julian Hsieh, Shari Shuchmann, Ferenc Nagy,
Harald te Nijenhuis, and David Mordo*

Novellus Systems, San Jose, California 95134, USA

ABSTRACT

The effects of nitrous oxide plasma surface treatment of fluorinated silica glass (FSG) films were investigated to improve film stability and adhesion properties. FSG films with varying fluorine concentrations were deposited using plasma-enhanced chemical vapor deposition (PECVD), then exposed to a nitrous oxide plasma to modify the surface. Treated films were boiled to study the moisture absorption, and subsequent depositions of foreign passivation films such as silicon nitride, silicon oxynitride, etc., were used to study the changes in adhesion characteristics. It was found that plasma treatments under certain conditions could enhance the adhesion characteristics of films with higher fluorine dopant levels, but did not measurably change the moisture resistance of the films. The effects of the plasma treatment were confined to the surface and did not measurably effect the bulk properties of the film. The effects of the nitrous oxide plasma treatment of PECVD FSG films are presented along with proposed mechanisms to explain the effects.

Introduction

Plasma-enhanced chemical vapor deposited (PECVD) fluorinated silica glass (FSG) films are attractive in both intermetal dielectric (IMD) and passivation applications due to their lower dielectric constant and improved step coverage over undoped tetraethylorthosilicate (TEOS) oxide films. The physical properties and gap fill capabilities of FSG films are dependent on the fluorine levels in the film; increasing the fluorine content improves the step coverage and gap fill while simultaneously reducing the dielectric constant. However, FSG films with high levels of fluorine incorporation have been shown to be unstable, both to moisture absorption and to dielectric constant stability.¹⁻⁴ Moisture absorption increases the dielectric constant due to the high polarizability of freely bonded (interstitial) water and silanol (Si-OH) in the film. In addition, films that are good diffusion barriers to gases and moisture (passivation and metal films) have indicated some adhesion issues when deposited on highly doped FSG films.

We have shown that as-deposited FSG films with dielectric constants as low as 3.5 are stable against moisture absorption.⁵ At this level of dopant concentration, there is also excellent gap fill of structures up to 1.35:1 aspect ratio at 0.35 μm .⁶ However, to extend the FSG to fill more aggressive structures and further decrease the dielectric constant, the fluorine content in the film must be increased to the point where the film becomes unstable. At high fluorine levels, subsequent depositions of passivation or metal films, including silicon nitride (SiN), silicon oxynitride (SiON), and titanium nitride (TiN), have shown blistering at the interface of the FSG.

The use of nitrogen- and oxygen-containing plasmas to stabilize the dielectric constant of FSG films has been reported previously by Takeishi *et al.*^{7,8} Unlike previous work, we did not see any change in the moisture resistance of the FSG after plasma treatment; we found moisture resistance to be a function solely of the fluorine levels in the film, and the stability of the electrical properties was not modified by the plasma treatment. However, we did find some improvement in the adhesion of passivation films to highly doped FSG films after nitrous oxide plasma exposure. Here, we extend the use of nitrous oxide plasmas to address adhesion issues with highly doped FSG films.

Experimental

The FSG films were deposited in a Novellus Systems Concept One Maxus PECVD reactor. The Concept One Maxus is a multistation sequential deposition PECVD reactor using a $\text{TEOS} + \text{O}_2 + \text{C}_2\text{F}_4$ chemistry. The system is capable of dual frequency operation at high total power

and high ratios of low frequency to total power (high-frequency (HF, 13.56 MHz) radio frequency (RF) power plus low frequency (LF, 400 kHz) RF power). Details of the process system and configuration have been reported elsewhere.⁹ This system is capable of total power levels exceeding 2.0 kW with LF/total power ratios up to 0.9 (90% LF power). This system also allows increased process gas flows [up to 18 standard liters per minute (slm) O_2 and 3 slm C_2F_4] at low (1.5 to 3.5 Torr) pressures. The process conditions for the deposition of the FSG films varied depending on the targeted fluorine concentration for the film. TEOS flows ranged from 1.0 to 3.5 ml/min. C_2F_4 flows ranged from 1.0 to 3.5 slm. Pressure, total power, % LF power, and O_2 flows were fixed at 2.6 Torr, 2.3 kW, 75% LF, and 18 slm, respectively.

Initial tests of the N_2O plasma were run at 350°C, 5 slm N_2O , 2.6 Torr, and 1.0 kW total power, HF only. The only variable tested was plasma treatment time. After initial testing, experiments were designed to define an optimal process. The optimal process was defined as a process which allowed a 1 μm SiN film to be deposited on an N_2O plasma-treated 3% Si-F FSG film with no blistering or other evidence of adhesion problems. Variables included LF/total power ratio, pressure, temperature, N_2O flow, and total anneal time. Total power was fixed at 1.5 kW. Temperature was set at 350 and 400°C. LF/total power was varied from 0 to 0.7 (70% LF power). Total deposition time ranged from 60 to 2000 s. Gas flow and pressure were combined into a single variable, residence time (Table I), which is an estimate of the average time the gas molecules remain in the reactor chamber. All the films were deposited on 200 mm silicon wafers. After plasma treatment, adhesion properties were tested with 1 μm SiN films deposited at 400°C (2.04 refractive index, 1.5 Gdyn/cm² compressive stress). Refractive index (RI) was measured using a Metricon prism coupler. Film stress was measured with an FSM 8800 stress measurement gauge. The fluorine content of the films was measured by Fourier transform infrared spectroscopy (FTIR), and is expressed as Si-F%, which is defined as the integral area of the Si-F peak ($\sim 937 \text{ cm}^{-1}$) normalized to the area of the Si-O peak ($\sim 1090 \text{ cm}^{-1}$) and corrected for effects of film thickness.¹⁰ The gap fill capabilities and blistering of the FSG films

Table I. Residence time (average time for N_2O to remain in reactor chamber).

Residence time	Estimated residence time (s)	N_2O flow (slm)	Pressure (Torr)
Short	6.6	4.0	3.0
Long	30.9	2.0	7.0

* Electrochemical Society Active Member.

was measured using cross-sectional scanning electron microscopy (SEM). The nitrogen incorporation from the plasma treatment was measured using quadrupole secondary ion mass spectroscopy (SIMS). Measurements of fluorine evolution were made using an MTM Engineering thermal desorption spectrometer (TDS).

Results and Discussion

Film adhesion.—Initial tests indicated that any exposure to N_2O plasmas of a 3% Si-F FSG film before SiN deposition improved the adhesion of the SiN. Controls run without plasma treatment showed blistering over the entire surface. Figure 1 is a SEM photograph of an SiN film peeling from a 3% Si-F FSG film, showing the SiN peeling at the SiN/FSG interface. This most likely is due to thermal desorption of water and HF from the FSG during SiN desorption. Desorbed water can be either interstitial water or silanol and fluorine that has reacted with the hydrogen in the SiN chemistry, forming water and HF. Desorbed species become trapped beneath the SiN and reduce the adhesion, leading to the blistering. Thermal desorption analysis of FSG films before and after plasma treatment show substantially different spectra. Figures 2a and b are TDS spectra of untreated and plasma-treated FSG films, respectively. The untreated film shows a broad peak at $\sim 200^\circ\text{C}$ for mass number 18, which is likely due to interstitial (absorbed unbonded) water desorbing from the film. The second peak for mass number 18 at $\sim 400^\circ\text{C}$ is most likely due to reactions such as $\text{Si} - \text{OH} \rightarrow \text{Si}^\cdot + \text{H}_2\text{O}$. Both of these peaks are absent from the plasma-treated spectra. The untreated spectra also shows a large peak at $\sim 400^\circ\text{C}$ for mass number 20, HF, which is absent from the treated spectra. Since the SiN deposition is performed at 400°C , this data implicates desorbed water and HF as the mechanism for film adhesion failure. However, since the plasma treatment is at 350°C , the mechanism for the improvement is not simply annealing of the FSG. A more likely mechanism is that the nitrogen from the plasma treatment getters hydrogen from the FSG by forming

N-H bonds at the surface; the gettering and binding of hydrogen results in a lack of hydrogen to react with fluorine and silanol in the FSG to form HF or water and results in a hydrophobic surface. This mechanism suggests that other methods of gettering hydrogen at the FSG surface will also result in improved adhesion for SiN films. This has been tested by the deposition of a 750 Å silane-based silicon-rich oxide (SRO, refractive index 1.50, O:Si ratio <2:1) in place of the nitrous oxide plasma. SRO films contain a substantial number of unterminated silicon bonds, which quickly getter available hydrogen to form strong Si-H bonds. SiN films deposited on 3% Si-F FSG films capped with the SRO did not blister. Additionally, unterminated Si bonds at the surface of the FSG can be terminated with N from the N_2O plasma to form a thin SiN layer at the surface of the FSG, which will prevent reactions of silanol and fluorine in the FSG with the hydrogen present in the subsequent SiN deposition chemistry.

Wafers run with a 60 s plasma exposure showed blistering only at the edge and bevel, and wafers exposed for 200 s did not blister after SiN deposition. Generally, long residence times were better (less blisters) than short residence times, but the difference was not dramatic. Any addition of LF power increased the amount of blistering somewhat. Since the total RF power was kept constant, the increase in blistering with increasing LF power is likely due to the decrease in the amount of HF power available to break up the N_2O molecules and to drive the surface

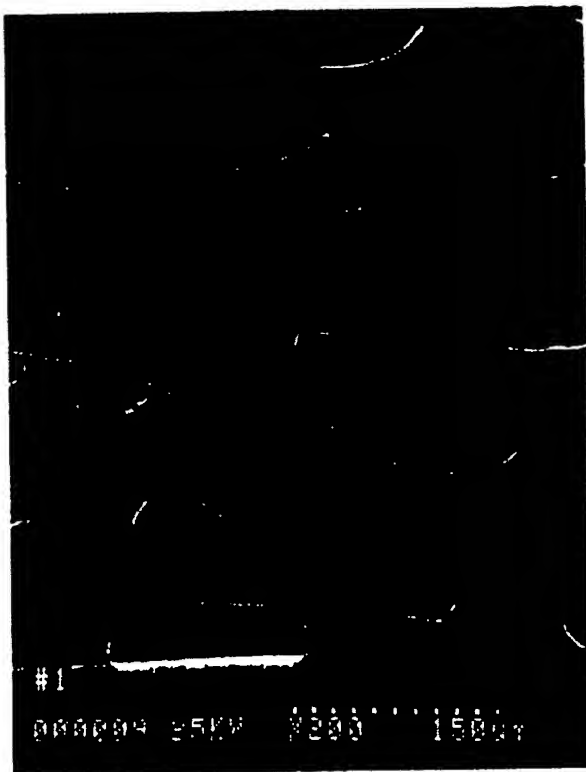


Fig. 1. SEM of blisters at an SiN-FSG interface.

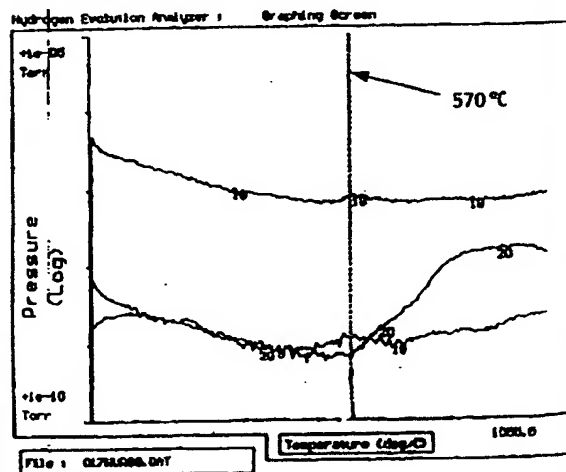
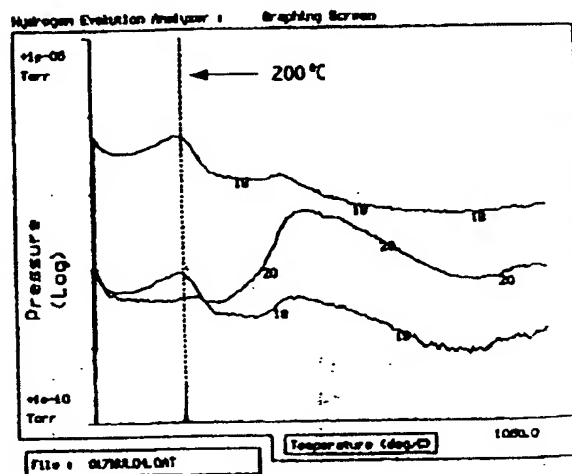


Fig. 2. TDS Spectra of (a, top) a 3% Si-F FSG film, as deposited and (b, bottom) TDS Spectra of an N_2O plasma-treated 3% Si-F FSG film.

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reactions. Increasing the temperature of the plasma treatment to 400°C dramatically worsened the adhesion, with some wafers suffering heavy blistering and peeling of the SiN from the FSG. This can be explained as follows: as proposed in the preceding section, the plasma treatment at 350°C getters hydrogen to reduce the formation of HF and water species which can desorb at 400°C during SiN deposition and be trapped under the SiN film. At 400°C, however, the HF and water desorb concurrently with the hydrogen gettering, resulting in gettering of hydrogen from the FSG and the formation of a poor quality SiN layer at the FSG surface, which can then fail during the subsequent SiN deposition. Increasing the exposure time beyond 200 s had no measurable effect until the exposure time reached 1000 s. Above 1000 s, FSG films blistered during plasma treatment, before the SiN deposition. This is possibly due to blanket SiN formation at the surface of the FSG, although this phenomenon is not well understood. An optimal process was defined as 1.5 kW total power (0% LF), 350°C, long residence time, and 200 s total deposition time.

Films receiving various plasma treatments were left out in open air for 2 days before SiN deposition. All films, regardless of treatment, blistered during SiN deposition. This is due to prolonged exposure to moisture allowing the formation of HF and SiOH at the surface, eliminating the effectiveness of the plasma treatment. The thin SiN layer formed at the surface is an insufficient barrier to stop the diffusion of environmental moisture into the film. FSG films left in atmosphere for 2 days prior to plasma treatment also showed blistering in all cases. This phenomenon is not understood, but is likely related. The optimal process plasma treatment resolves the adhesion problems of the FSG film as long as the time intervals between the FSG/plasma treatment and the subsequent deposition are short enough.

Changes to bulk material.—Experiments were run to show that there are no bulk changes in the film resulting from the plasma treatment. Takeishi *et al.*, indicated that long enough plasma exposures resulted in nitrogen diffusion throughout the bulk of the film.⁹ Although no changes in the bulk properties of the film were expected to occur, experiments were run to confirm this supposition. FSG films with 3% Si-F were exposed to the optimal process treatment. Figures 3a and b are SEM cross sections of patterned wafers run with and without plasma treatment. As expected there are no differences between the two photographs, indicating that there are no changes in the step coverage or gap fill due to the plasma treatment. Figures 4a and b are SIMS depth profiles of plasma-treated FSG films capped with SiN, showing the surface nature of the Si-N in the FSG layer. Figure 4c is a SIMS depth profile of an untreated FSG film capped with SiN. The nitrogen levels are higher in the untreated film, while the nitrogen diffusion is both lower in magnitude and falls off to noise levels within 1500 to 2000 Å in the plasma-treated films. This supports the hypothesis that a thin SiN layer is formed at the surface of the FSG during the nitrous oxide plasma treatment, and that this layer prevents further diffusion of nitrogen into the FSG during the subsequent SiN deposition. RI, stress, and Si-F% were measured before and after plasma treatment. Results of these measurements are shown in Table II.

The differences between the treated and untreated films were very small. In all cases, the RI and Si-F% showed a smaller change for the treated films than for controls. The stress did become less compressive in all cases. This may be due to a thermal hysteresis effect, as the wafers were cooled and exposed to atmosphere between FSG deposition and plasma treatment. This cooling and exposure was necessary to measure the before-treatment properties of the FSG films. The before and after values of Si-F% for the first two wafers are the same within the accuracy of the measurement. The Si-F% differences for the two highly doped films are real; highly doped films are known to be

unstable. Figure 5 is an FTIR spectra of the Si-F peak, before and after plasma treatment. Since the peak height and area is unchanged, it is clear that the fluorine driven off is not bound in the film. This is supported by before and after RI measurements, which also show no change, indicating the bulk properties of the film are not affected

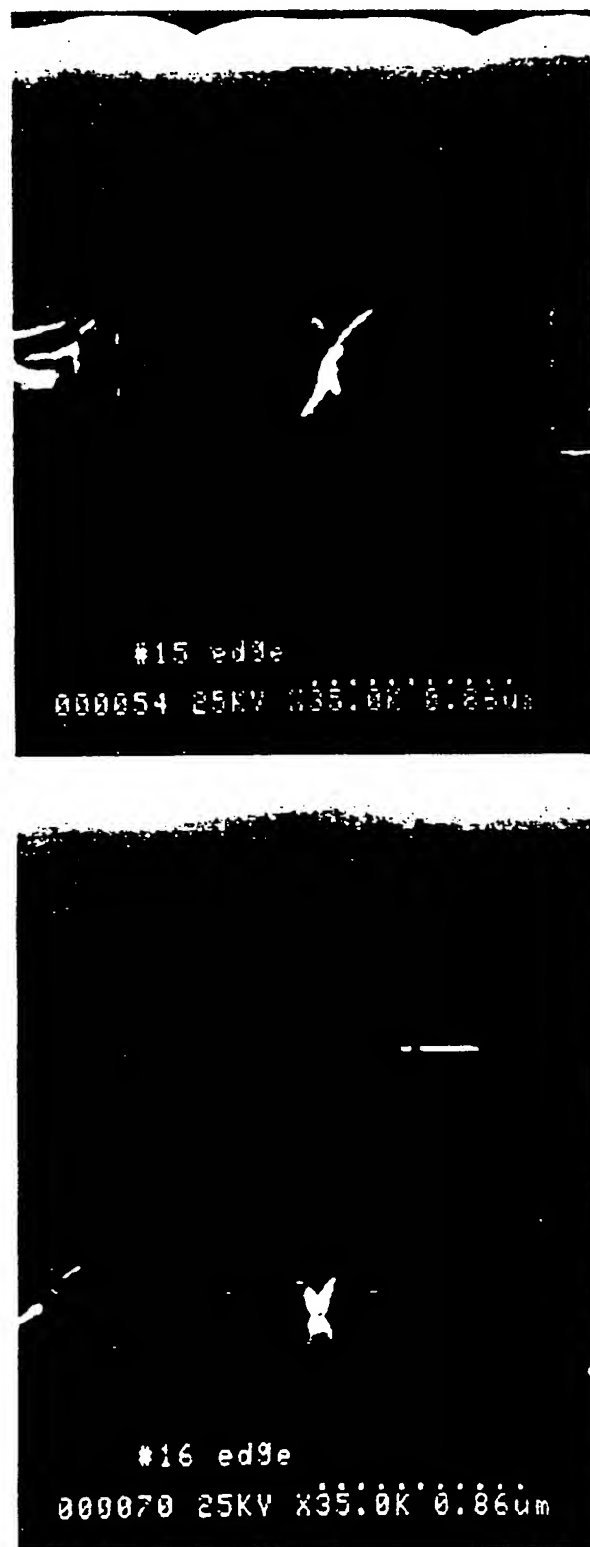


Fig. 3. SEM cross section of a 3% Si-F FSG film: (a, top) as deposited and (b, bottom) treated with N_2O plasma and capped with SiN.

by the plasma treatment. This is a ~3% Si-F film; films with higher levels of fluorine doping do show changes in the Si-F peak height and area before and after plasma treatment. Figure 6 is an FTIR subtraction spectra of a 3%

Si-F FSG film before and after plasma treatment. The small peaks in the region of the Si-O and Si-F bond peaks are a result of the limited resolution of the FTIR and are not real changes in the peaks. The significant factor in this

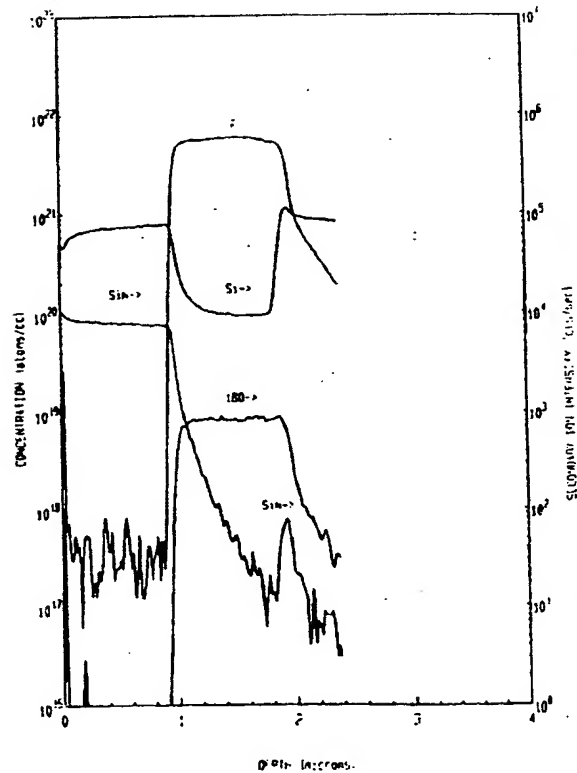
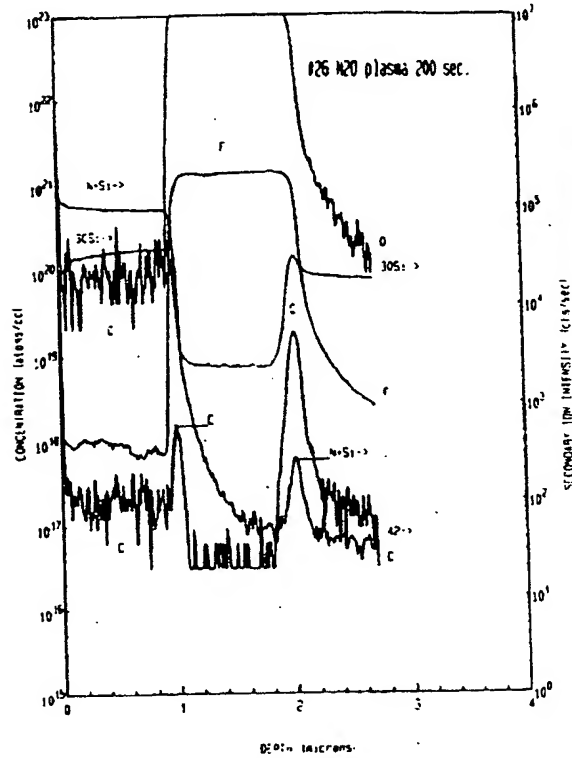
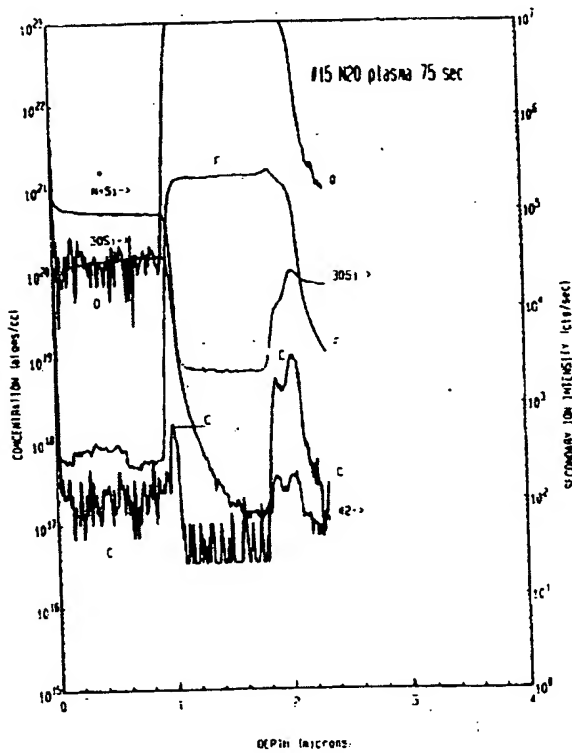


Fig. 4. SIMS depth profile of a 3% FSG film: (a, above) 75 s N_2O plasma exposure and capped with 1 μm SiN; (b, top right) 200 s N_2O plasma exposure, and capped with 1 μm SiN; and (c, right) capped with a 1 μm SiN film, without N_2O plasma exposure.

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Table II. Physical properties of FSG films, before and after N_2O plasma treatment.

Water	Refractive index, before	Refractive index, post	Stress, before treatment (Gdyn/cm ²)	Stress, post treatment (Gdyn/cm ²)	Si-F% before	Si-F% post
1	1.4113	1.4133	-0.66	-0.57	3.05	2.96
2	1.4251	1.4256	-1.19	-1.07	2.59	2.52
3	—	—	-0.11	-0.05	5.95	5.37
4	1.3786	1.3873	0.43	0.25	7.88	7.00

Table III. Moisture stability of physical properties of FSG films, with and without N_2O plasma treatment.

Plasma Treatment								
Boiling	Refractive index							
	C-1	T-2	C-2	T-2	C-3	T-3	C-4	T-4
Before	1.4313	1.4306	1.4251	1.4263	—	—	1.3786	1.3811
After	1.4347	1.4331	1.4331	1.4281	—	—	1.4189	1.4205
Delta	0.0034	0.0028	0.0022	0.0018	—	—	0.0403	0.0394
Boiling	Film stress (Gdyn/cm ²)							
	C-1	T-2	C-2	T-2	C-3	T-3	C-4	T-4
Before	-0.66	-0.66	-1.19	-1.15	-0.11	-0.15	0.43	0.46
After	-0.76	-0.86	-1.29	-1.52	-0.30	—	0.30	0.47
Delta	0.10	0.20	0.10	0.37	0.19	—	0.13	0.01
Boiling	Si-F%							
	C-1	T-2	C-2	T-2	C-3	T-3	C-4	T-4
Before	3.05	2.99	2.59	2.49	5.95	5.62	7.88	8.08
After	3.02	3.03	2.50	2.49	4.57	4.85	4.51	4.50
Delta	0.03	0.04	0.09	0.00	1.38	0.77	3.37	3.58

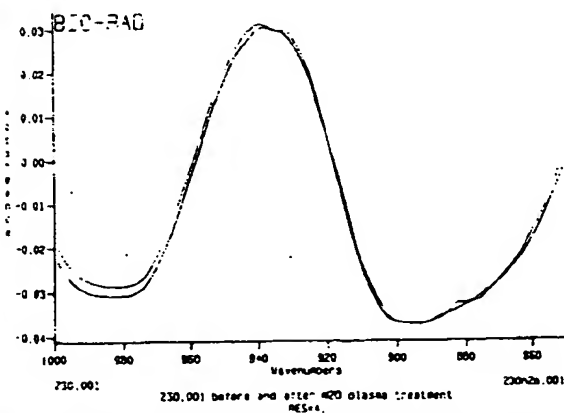
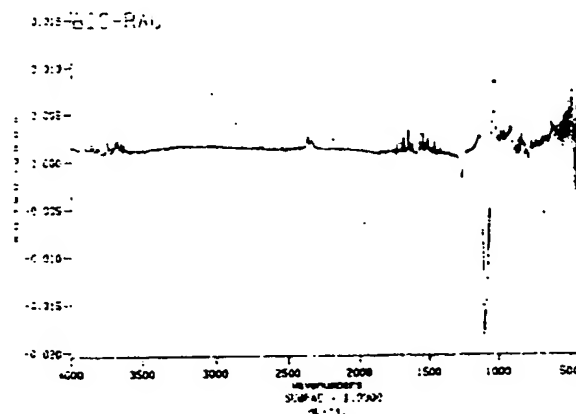
C = control (no plasma treatment), T = plasma treated.

spectra is the complete lack of change in the Si-OH (3600 cm⁻¹) peak. This indicates that the bulk silanol in the film has not changed.

To further study the nature of the plasma treatment, films were produced by depositing five layers of FSG, each layer 0.2 μ m thick, followed by a 40 s plasma treatment (0.2 total time for the optimum process condition defined earlier) for each layer. Takeishi *et al.*, showed optimum moisture resistance after a 30 min plasma treatment, this time being long enough to distribute nitrogen throughout the film.⁴ Since long plasma treatments led to blistering on our films, we attempted to distribute nitrogen through the film using this multilayer process. Figure 7 is a SIMS depth profile of the multilayer film. Each of the five plasma treatments can be seen as dips in the atomic concentration for hydrogen and fluorine and increases in the secondary ion intensity for silicon and nitrogen. The loss of hydrogen and fluorine can be explained by the breaking of Si-H bonds in the FSG. Silicon is then free to recombine

with nitrogen to form Si-N at the surface, while the freed hydrogen can combine with loosely bound fluorine species to create HF at the surface, which can be desorbed. The depth profile also clearly shows the surface nature of the plasma treatment, as the increase in the nitrogen levels is confined to a depth of ~ 0.05 μ m at each interface. The multilayer films were left in air for 2 h, 1 day, and 2 days before being capped with SiN. All the films showed heavy blistering of the nitride. This is further evidence that the plasma treatment effects are confined to the surface, as the multilayer film behaved as if it were a single 1 μ m 3% Si-F film exposed to a 40 s N_2O plasma.

Moisture resistance.—FSG films were tested for moisture resistance by submerging in boiling water and measuring the changes in RI, stress, Si-F%, and silanol and water content. Films ranging from 2.6 to 7.9% Si-F were exposed to the optimal process treatment and boiled in water for 60 min. Measurements of various properties are shown in Table III. The uncertainty in the RI is ± 0.002 , the

Fig. 5. FTIR Si-F peak before and after 200 s N_2O plasma exposure.Fig. 6. FTIR subtraction spectra, 3% Si-F FSG film before and after 200 s N_2O plasma exposure.

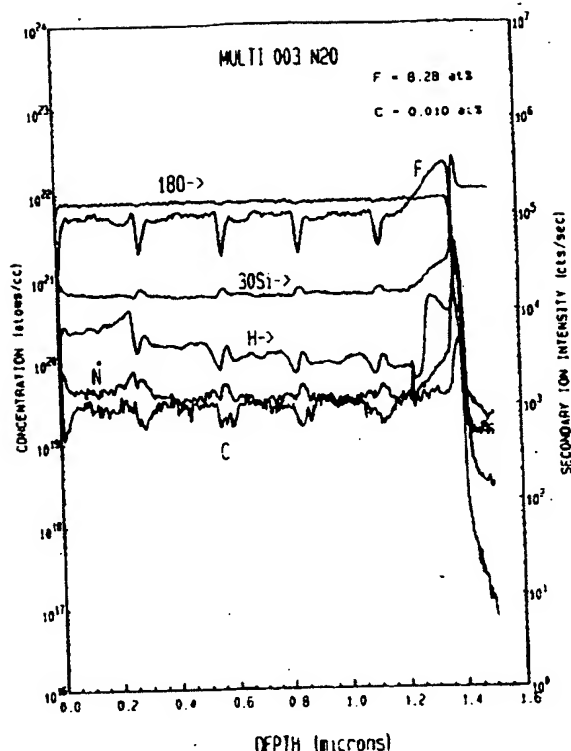


Fig. 7. SIMS depth profile of 3% Si-F FSG/40 s N₂O plasma multilayer film.

uncertainty in the stress is ± 0.1 Gdyne/cm², and the uncertainty in the Si-F% is ± 0.25 . By comparing the deltas between the before and after boiling measurements for each pair of wafers, it is clear that the plasma treatment has no significant effect on the moisture resistance of the films. The only measurable differences are in the stress measurements; however, data from Table II show that there are stress changes associated with the plasma treatment that are not related to the moisture resistance. Additionally, the mechanism for stress changes in tensile films is not understood: for tensile films, RI is a better indicator of film stability. These measurements are consistent with stability studies we have published previously that show no change in physical or electrical properties for films with as-deposited stress >0.5 Gdyne/cm² compressive, or with Si-F% $<4\%$.³ Figures 8a and b are FTIR spectra of the silanol (SiOH, ~ 3700 cm⁻¹) and water (~ 3400 cm⁻¹) peaks, before and after boiling and with and without plasma treatment. The change in the silanol content is lower for the plasma treated film, but the difference is not significant. These results indicate that moisture resistance of the FSG films is dependent on the as-deposited stress and Si-F content, and is not measurably affected by plasma treatments.

Conclusions

FSG films were exposed to nitrous oxide plasmas to enhance moisture resistance and to eliminate adhesion problems with subsequent depositions. Highly doped FSG films had no adhesion problems when the subsequent depositions occurred shortly after FSG deposition and plasma treatment. However, all films blistered after being exposed to air for 2 days before passivation deposition. There is no evidence that the moisture resistance of these FSG films was substantially improved by the N₂O plasma treatment. The plasma treatment is a surface effect, causing no changes in the bulk properties of the FSG.

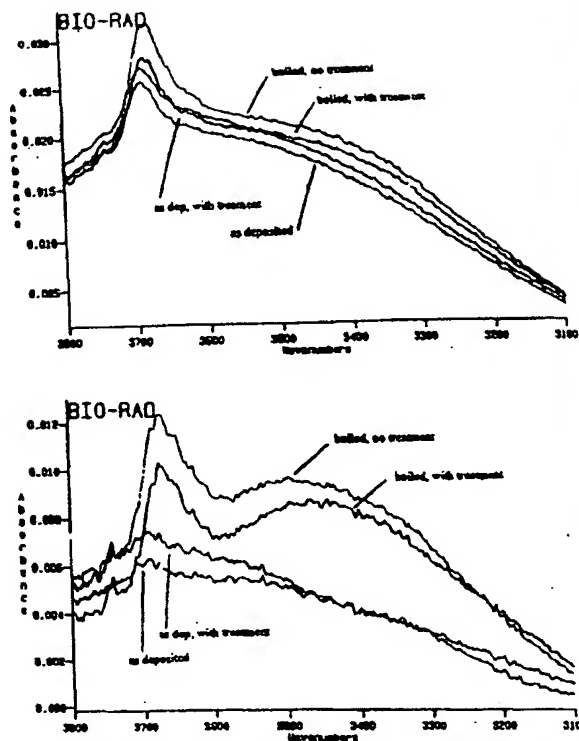


Fig. 8. FTIR water/SiOH peaks: (a, top) 3% Si-F FSG film before and after 60 min in boiling water, with and without plasma treatment; and (b, bottom) FTIR water/SiOH peaks, 5% Si-F FSG film before and after 60 min in boiling water, with and without plasma treatment.

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